

CLAIMS

We claim:

- 1 1. A method of performing atomic layer deposition comprising:
 - 2 pretreating a surface of a substrate to make the surface of the substrate reactive for
 - 3 performing atomic layer deposition;
 - 4 introducing a first precursor to deposit a first reactive species on the surface of the
 - 5 substrate, the pretreated surface being more receptive to having chemical termination sites
 - 6 for depositing the first reactive species, due to said pretreating the surface; and
 - 7 introducing a second precursor to have a second reactive species react with the
 - 8 deposited first reactive species.
- 1 2. The method of claim 1 further including forming a uniform film layer of 50
- 2 angstroms or less in thickness.
- 1 3. The method of claim 1 wherein said pretreating is performed by a plasma process.
- 1 4. The method of claim 1 wherein said pretreating the surface includes introducing a
- 2 radical species to attach to the surface of the substrate to increase termination sites for the
- 3 first reactive species.
- 1 5. The method of claim 4 wherein said pretreating is performed by a plasma process.

1 6. The method of claim 1 wherein said pretreating the surface includes introducing a
2 radical species to exchange bonds at the surface of the substrate to increase termination
3 sites for the first reactive species.

1 7. The method of claim 6 wherein said pretreating is performed by a plasma process.

1 8. The method of claim 1 wherein said pretreating the surface includes depositing an
2 intermediate layer on the substrate prior to introducing the first precursor, in which the
3 intermediate layer provides more termination sites for the first reactive species than the
4 substrate or where the substrate cannot be made reactive to atomic layer deposition.

1 9. The method of claim 8 wherein said pretreating is performed by a plasma process.

1 10. The method of claim 8 wherein said pretreating is performed by an atomic layer
2 deposition plasma process.

1 11. The method of claim 1 wherein said pretreating the surface includes introducing a
2 radical species to leach molecules from the substrate to increase termination sites for the
3 first reactive species.

1 12. The method of claim 11 wherein said pretreating is performed by a plasma
2 process.

1 13. The method of claim 1 wherein Al_2O_3 is deposited on silicon by atomic layer
2 deposition in which said pretreating includes introducing $\text{O}_2/\text{H}_2/\text{H}_2\text{O}/\text{NH}_3$ plasma to form

3 a layer of silicon oxide or silicon oxinitride, in which OH or NH_x group forms the
4 chemical termination sites on silicon.

1 14. The method of claim 1 wherein Al₂O₃ is deposited on silicon by atomic layer
2 deposition in which said pretreating includes forming a layer of SiO₂ that is hydroxilated
3 by exposing HF cleaned silicon to a pulse of H₂O to form the chemical termination sites
4 on silicon.

1 15. The method of claim 1 wherein Al₂O₃ is deposited on WN_x by atomic layer
2 deposition in which said pretreating includes introducing NH₃/H₂/N₂ plasma to leach
3 fluorine from WN_x to form NH_x as the chemical termination sites on WN_x.

1 16. The method of claim 1 wherein Al₂O₃ is deposited on TiN by atomic layer
2 deposition in which said pretreating includes introducing NH₃/H₂/N₂ plasma to form NH_x
3 as the chemical termination sites on TiN.

1 17. The method of claim 1 wherein Al₂O₃ is deposited on Ti by atomic layer
2 deposition in which said pretreating includes introducing NH₃/H₂/N₂ plasma to nitridize
3 the surface to form NH_x as the chemical termination sites on Ti.

1 18. The method of claim 1 wherein Al₂O₃ is deposited on W by atomic layer
2 deposition in which said pretreating includes introducing NH₃/H₂/N₂ plasma to nitridize
3 the surface to form NH_x as the chemical termination sites on W.

1 19. The method of claim 1 wherein Al_2O_3 is deposited on Ta by atomic layer
2 deposition in which said pretreating includes introducing $\text{NH}_3/\text{H}_2/\text{N}_2$ plasma to nitridize
3 the surface to form NH_x as the chemical termination sites on Ta.

1 20. The method of claim 1 wherein Al_2O_3 is deposited on Ta_xN by atomic layer
2 deposition in which said pretreating includes introducing $\text{NH}_3/\text{H}_2/\text{N}_2$ plasma to form NH_x
3 as the chemical termination sites on Ta_xN .

1 21. The method of claim 1 wherein Ta_2O_5 is deposited on Al_2O_3 by atomic layer
2 deposition in which said pretreating includes introducing $\text{O}_2/\text{H}_2/\text{H}_2\text{O}$ plasma to form OH
3 species as the chemical termination sites on Al_2O_3 .

1 22. The method of claim 1 wherein Al_2O_3 is deposited on Ta_2O_5 by atomic layer
2 deposition in which said pretreating includes introducing $\text{O}_2/\text{H}_2/\text{H}_2\text{O}$ plasma to form OH
3 species as the chemical termination sites on Ta_2O_5 .

1 23. The method of claim 1 wherein TiO_x is deposited on Al_2O_3 by atomic layer
2 deposition in which said pretreating includes introducing $\text{O}_2/\text{H}_2/\text{H}_2\text{O}$ plasma to form OH
3 species as the chemical termination sites on Al_2O_3 .

1 24. The method of claim 1 wherein Al_2O_3 is deposited on TiO_x by atomic layer
2 deposition in which said pretreating includes introducing $\text{O}_2/\text{H}_2/\text{H}_2\text{O}$ plasma to form OH
3 species as the chemical termination sites on TiO_x .

1 25. The method of claim 1 wherein TiO_x is deposited on TiN by atomic layer
2 deposition in which said pretreating includes introducing $NH_3/H_2/N_2$ plasma to form NH_x
3 species as the chemical termination sites on TiN.

1 26. The method of claim 1 wherein W is deposited on TiN by atomic layer deposition
2 in which said pretreating includes introducing $NH_3/H_2/N_2$ plasma to form NH_x species as
3 the chemical termination sites on TiN.

1 27. The method of claim 1 wherein WN_x is deposited on TiN by atomic layer
2 deposition in which said pretreating includes introducing $NH_3/H_2/N_2$ plasma to form NH_x
3 species as the chemical termination sites on TiN.

1 28. The method of claim 1 wherein WN_x is deposited on SiO_2 by atomic layer
2 deposition in which said pretreating includes introducing $O_2/H_2/H_2O$ plasma to form OH
3 species that are reactive with $TiCl_4$ and in which the $TiCl_4$ is used to grow an intermediate
4 layer of Ti or TiN to form NH_x as the chemical termination sites on Ti or TiN.

1 29. The method of claim 1 wherein W is deposited on SiO_2 by atomic layer deposition
2 in which said pretreating includes introducing $O_2/H_2/H_2O$ plasma to form OH species that
3 are reactive with $TiCl_4$ and in which the $TiCl_4$ is used to grow an intermediate layer of Ti
4 or TiN to form NH_x as the chemical termination sites on Ti or TiN.

1 30. The method of claim 1 wherein W is deposited on SiO_2 by atomic layer deposition
2 in which said pretreating includes introducing $O_2/H_2/H_2O$ plasma to form OH species that

3 are reactive with $TaCl_5$ and in which the $TaCl_5$ is used to grow an intermediate layer of
4 Ta_xN to form NH_x as the chemical termination sites on Ta_xN .

1 31. The method of claim 1 wherein WN_x is deposited on hydrocarbon polymer by
2 atomic layer deposition in which said pretreating includes introducing NF_3 plasma to
3 generate fluorine atoms that leach hydrogen from the hydrocarbon polymer and in which
4 the leached surface is reacted with $TiCl_4$ to grow an intermediate layer of TiN or a
5 combination of Ti/TiN to form NH_x as the chemical termination sites on TiN or Ti/TiN.

1 32. The method of claim 1 wherein WN_x is deposited on perfluorocarbon polymer by
2 atomic layer deposition in which said pretreating includes introducing H_2/NH_3 plasma to
3 generate hydrogen atoms and NH_x radicals that leach fluorine from the hydrocarbon
4 polymer and in which the leached surface is reacted with $TiCl_4$ to grow an intermediate
5 layer of TiN or a combination of Ti/TiN to form NH_x as the chemical termination sites on
6 TiN or Ti/TiN.

1 33. The method of claim 1 wherein a second oxide is deposited on a first oxide by
2 atomic layer deposition in which said pretreating includes introducing $O_2/H_2/H_2O$ plasma
3 to activate the first oxide and to terminate the surface with OH species that are reactive
4 with a metal precursor for the second oxide layer.

1 34. The method of claim 1 wherein an oxide is deposited on metal, semiconductor or
2 metal nitride by atomic layer deposition in which said pretreating includes introducing
3 $NH_3/H_2/N_2$ plasma to terminate the surface with NH_x species that are reactive with a
4 metal precursor.

1 35. The method of claim 1 wherein a metal, semiconductor or conductive metalnitride
2 is deposited on oxide by atomic layer deposition in which said pretreating includes
3 introducing NH₃/H₂/N₂ plasma which is used to terminate the surface with NH_x species.

1 36. The method of claim 1 wherein a metal, semiconductor or conductive metalnitride
2 is deposited on oxide by atomic layer deposition in which said pretreating includes
3 introducing O₂/H₂/H₂O plasma generated radicals which are used to terminate the surface
4 with OH species.

1 37. An apparatus for performing atomic layer deposition comprising:
2 a processing chamber for subjecting a substrate to atomic layer deposition to
3 deposit a film layer;
4 a mixing manifold for mixing chemicals with a carrier gas, said mixing manifold
5 coupled to said processing chamber for delivery of a first precursor chemical during a
6 first time period and delivery of a second precursor chemical during a second period to
7 generate a first and second plasma, respectively, to perform atomic layer deposition to
8 deposit the film layer;
9 said mixing manifold also coupled to receive a pretreating chemical specie for
10 coupling into said processing chamber prior to introduction of the first and second
11 precursor chemicals, said pretreating chemical specie introduced into said processing
12 chamber to pretreat the substrate surface to make its surface more reactive to the first
13 precursor chemical.

1 38. The apparatus of claim 37 wherein said pretreating chemical specie introduces a
2 radical species to attach to the surface of the substrate to increase termination sites for the
3 first precursor chemical.

1 39. The apparatus of claim 37 wherein said pretreating chemical specie introduces a
2 radical species to exchange bonds at the surface of the substrate to increase termination
3 sites for the first precursor chemical.

1 40. The apparatus of claim 37 wherein said pretreating chemical specie deposits an
2 intermediate layer on the substrate prior to introducing the first precursor chemical, in
3 which the intermediate layer provides more termination sites for the first precursor
4 chemical or where the substrate cannot be made reactive to atomic layer deposition.

1 41. The apparatus of claim 37 wherein said pretreating chemical specie introduces a
2 radical species to leach molecules from the substrate to increase termination sites for the
3 first precursor chemical.

1 42. A method to perform atomic layer deposition comprising:
2 pretreating a surface of a substrate or a material layer formed on the substrate by
3 introducing a radical specie including any combination of O₂, H₂, H₂O, NH₃, NF₃, N₂, Cl
4 and F to increase AH_x termination sites on the surface, where x is an integer and A is a
5 non-metal capable of bonding with hydrogen H;

6 introducing a first precursor to deposit a first reactive specie on the surface, the
7 surface when pretreated being more receptive to have additional bonding with the first
8 reactive specie, due to the increase of AHx termination sites on the surface; and

9 introducing a second precursor, after the bonding of the first reactive specie, to
10 deposit a second reactive specie to react with the deposited first reactive specie to form a
11 film layer.

1 43. The method of claim 42 further including forming the film layer to have a
2 thickness of 50 angstroms or less by repeatedly introducing the first precursor followed
3 by the second precursor.

1 44. The method of claim 42 wherein said pretreating the surface includes introducing
2 the radical specie to exchange bonds at the surface of the substrate to increase AHx
3 termination sites for the first reactive specie.

1 45. The method of claim 42 wherein said pretreating the surface forms NHx
2 termination sites.

3 46. The method of claim 42 further comprising forming an intermediate layer on the
4 substrate prior to introducing the first precursor, wherein the radical specie is introduced
5 with the intermediate layer to increase termination sites for the first reactive specie.

1 47. The method of claim 42 wherein said pretreating the surface includes introducing
2 the radical specie to leach molecules from the substrate to increase termination sites for
3 the first reactive specie.

1 48. The method of claim 42 wherein said pretreating further includes introducing the
2 radical specie by plasma.

1 49. The method of claim 42 wherein said pretreating further includes introducing the
2 radical specie by plasma and the reactive species form the film layer, wherein the film
3 layer is comprised of a metal, metal oxide or metal nitride.

1 50. The method of claim 48 wherein Al_2O_3 is deposited on silicon by atomic layer
2 deposition in which said pretreating includes introducing $\text{O}_2/\text{H}_2/\text{H}_2\text{O}/\text{NH}_3$ plasma to form
3 a film layer of silicon oxide or silicon oxinitride, in which OH or NH_x group forms the
4 termination sites on silicon.

1 51. The method of claim 48 wherein Al_2O_3 is deposited on WN_y , where y is an
2 integer, by atomic layer deposition in which said pretreating includes introducing
3 $\text{NH}_3/\text{H}_2/\text{N}_2$ plasma to leach fluorine from WN_y to form NH_x as the termination sites on
4 WN_y .

1 52. The method of claim 48 wherein Al_2O_3 is deposited on TiN by atomic layer
2 deposition in which said pretreating includes introducing $\text{NH}_3/\text{H}_2/\text{N}_2$ plasma to form NH_x
3 as the termination sites on TiN.

1 53. The method of claim 48 wherein Al_2O_3 is deposited on Ti by atomic layer
2 deposition in which said pretreating includes introducing $\text{NH}_3/\text{H}_2/\text{N}_2$ plasma to nitridize
3 the surface to form NH_x as the termination sites on Ti.

1 54. The method of claim 48 wherein Al_2O_3 is deposited on W by atomic layer
2 deposition in which said pretreating includes introducing $\text{NH}_3/\text{H}_2/\text{N}_2$ plasma to nitridize
3 the surface to form NH_x as the termination sites on W.

1 55. The method of claim 48 wherein Al_2O_3 is deposited on Ta by atomic layer
2 deposition in which said pretreating includes introducing $\text{NH}_3/\text{H}_2/\text{N}_2$ plasma to nitridize
3 the surface to form NH_x as the termination sites on Ta.

1 56. The method of claim 48 wherein Al_2O_3 is deposited on Ta_yN , where y is an
2 integer, by atomic layer deposition in which said pretreating includes introducing
3 $\text{NH}_3/\text{H}_2/\text{N}_2$ plasma to form NH_x as the termination sites on Ta_yN .

1 57. The method of claim 48 wherein Ta_2O_5 is deposited on Al_2O_3 by atomic layer
2 deposition in which said pretreating includes introducing $\text{O}_2/\text{H}_2/\text{H}_2\text{O}$ plasma to form OH
3 specie as the termination sites on Al_2O_3 .

1 58. The method of claim 48 wherein Al_2O_3 is deposited on Ta_2O_5 by atomic layer
2 deposition in which said pretreating includes introducing $\text{O}_2/\text{H}_2/\text{H}_2\text{O}$ plasma to form OH
3 specie as the termination sites on Ta_2O_5 .

1 59. The method of claim 48 wherein TiO_z , where z is an integer, is deposited on
2 Al_2O_3 by atomic layer deposition in which said pretreating includes introducing
3 $\text{O}_2/\text{H}_2/\text{H}_2\text{O}$ plasma to form OH specie as the termination sites on Al_2O_3 .

1 60. The method of claim 48 wherein Al_2O_3 is deposited on TiO_z , where z is an
2 integer, by atomic layer deposition in which said pretreating includes introducing
3 $\text{O}_2/\text{H}_2/\text{H}_2\text{O}$ plasma to form OH specie as the termination sites on TiO_z .

1 61. The method of claim 48 wherein TiO_z , where z is an integer, is deposited on TiN
2 by atomic layer deposition in which said pretreating includes introducing $\text{NH}_3/\text{H}_2/\text{N}_2$
3 plasma to form NH_x specie as the termination sites on TiN.

1 62. The method of claim 48 wherein W is deposited on TiN by atomic layer
2 deposition in which said pretreating includes introducing $\text{NH}_3/\text{H}_2/\text{N}_2$ plasma to form NH_x
3 specie as the termination sites on TiN.

1 63. The method of claim 48 wherein WN_y , where y is an integer, is deposited on TiN
2 by atomic layer deposition in which said pretreating includes introducing $\text{NH}_3/\text{H}_2/\text{N}_2$
3 plasma to form NH_x specie as the termination sites on TiN.

1 64. The method of claim 48 wherein WN_y , where y is an integer, is deposited on SiO_2
2 by atomic layer deposition in which said pretreating includes introducing $\text{O}_2/\text{H}_2/\text{H}_2\text{O}$
3 plasma to form OH specie that are reactive with TiCl_4 and in which the TiCl_4 is used to
4 grow an intermediate layer of Ti or TiN to form NH_x as the termination sites on Ti or
5 TiN.

1 65. The method of claim 48 wherein W is deposited on SiO_2 by atomic layer
2 deposition in which said pretreating includes introducing $\text{O}_2/\text{H}_2/\text{H}_2\text{O}$ plasma to form OH

3 specie that are reactive with $TiCl_4$ and in which the $TiCl_4$ is used to grow an intermediate
4 layer of Ti or TiN to form NH_x as the termination sites on Ti or TiN.

1 66. The method of claim 48 wherein W is deposited on SiO_2 by atomic layer
2 deposition in which said pretreating includes introducing $O_2/H_2/H_2O$ plasma to form OH
3 specie that is reactive with $TaCl_5$ and in which the $TaCl_5$ is used to grow an intermediate
4 layer of Ta_zN , where z is an integer, to form NH_x as the termination sites on Ta_zN .

1 67. The method of claim 48 wherein WN_y , where y is an integer, is deposited on
2 hydrocarbon polymer by atomic layer deposition in which said pretreating includes
3 introducing NF_3 plasma to generate fluorine atoms that leach hydrogen from the
4 hydrocarbon polymer and in which the leached surface is reacted with $TiCl_4$ to grow an
5 intermediate layer of TiN or a combination of Ti/TiN to form NH_x as the termination sites
6 on TiN or Ti/TiN.

1 68. The method of claim 48 wherein WN_y , where y is an integer, is deposited on
2 perfluorocarbon polymer by atomic layer deposition in which said pretreating includes
3 introducing H_2/NH_3 plasma to generate hydrogen atoms and NH_x radicals that leach
4 fluorine from the hydrocarbon polymer and in which the leached surface is reacted with
5 $TiCl_4$ to grow an intermediate layer of TiN or a combination of Ti/TiN to form NH_x as the
6 termination sites on TiN or Ti/TiN.

1 69. The method of claim 48 wherein an oxide is deposited on metal, semiconductor or
2 metal nitride by atomic layer deposition in which said pretreating includes introducing

3 NH₃/H₂/N₂ plasma to terminate the surface with NH_x specie that are reactive with a metal
4 precursor.

1 70. The method of claim 48 wherein a metal, semiconductor or conductive metal
2 nitride is deposited as the film layer on oxide by atomic layer deposition in which said
3 pretreating includes introducing NH₃/H₂/N₂ plasma which is used to terminate the surface
4 with NH_x specie.

1 71. A method to perform atomic layer deposition comprising:
2 depositing an intermediate layer;
3 pretreating a surface of the deposited intermediate layer by introducing a radical
4 specie including any combination of O₂, H₂, H₂O, NH₃, NF₃, N₂, Cl and F to increase
5 AH_x termination sites on the surface, where x is an integer and A is a non-metal capable
6 of bonding with hydrogen H;

7 introducing a first precursor to deposit a first reactive specie on the surface, the
8 surface when pretreated being more receptive to have additional bonding with the first
9 reactive specie, due to the increase of AH_x termination sites on the surface; and
10 introducing a second precursor, after the bonding of the first reactive specie, to
11 deposit a second reactive specie to react with the deposited first reactive specie to form a
12 film layer.

1 72. A method to perform atomic layer deposition comprising:
2 leaching hydrogen or fluorine from a surface by pretreating the surface by
3 introducing a radical specie including any combination of O₂, H₂, H₂O, NH₃, NF₃, N₂, Cl

4 and F to increase AH_x termination sites on the surface, where x is an integer and A is a
5 non-metal capable of bonding with hydrogen H;
6 introducing a first precursor to deposit a first reactive specie on the surface, the
7 surface when pretreated being more receptive to have additional bonding with the first
8 reactive specie, due to the increase of AH_x termination sites on the surface; and
9 introducing a second precursor, after the bonding of the first reactive specie, to
10 deposit a second reactive specie to react with the deposited first reactive specie to form a
11 film layer.

1 73. A structure formed on a substrate comprising:
2 a material layer formed on the substrate in which the material layer is pretreated
3 by introducing a radical specie including any combination of O₂, H₂, H₂O, NH₃, NF₃, N₂,
4 Cl and F to increase AH_x termination sites on the surface of the material layer, where x is
5 an integer and A is a non-metal capable of bonding with hydrogen H;
6 a film layer formed above said material layer by repeated introduction of a first
7 precursor followed by a second precursor to deposit said film layer by atomic layer
8 deposition, the first precursor to deposit a first reactive specie on the surface of the
9 material layer, the surface when pretreated being more receptive to have additional
10 bonding with the first reactive specie, due to the increase of AH_x termination sites on the
11 surface and the second precursor to deposit a second reactive specie to react with the
12 deposited first reactive specie to form said film layer.